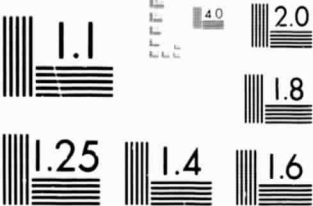


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ULTRAVIOLET RADIATION EFFECTS ON THE INFRARED DAMAGE RATE OF A THERMAL CONTROL COATING

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OF A THERMAL CONTROL COATING**

by
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Greenbelt, Maryland 20771**

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ULTRAVIOLET RADIATION EFFECTS ON THE INFRARED DAMAGE RATE OF A THERMAL CONTROL COATING

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INTRODUCTION

The degradation of the infrared reflectance of thermal control coatings by ultraviolet radiation has been previously studied by numerous researchers. The work of Colony* and Greenberg (Reference 1) is typical of the research; they obtained data on thermal-control coatings by the use of the gross spectral characteristics of a mercury light source. However, few simulated degradation experiments using monochromatic light at various intensities from this type of source have been performed on paints, their components, or other thermal-control coatings.

Arvesen (Reference 2) conducted experiments to determine the spectral sensitivity of selected thermal-control coatings: TiO_2 /epoxy, ZnO /methyl silicone (S-13), and $\text{ZnO}/\text{K}_2\text{SiO}_3$ (Z-93). The increase in solar absorptance per energy dose was used to evaluate the sensitivity of a coating to radiation in specific wavelength regions. Irradiations were performed in a vacuum with a high-intensity xenon arc lamp that was selectively filtered with bandpass and short-wavelength cutoff filters. Degradation in each case was found to be quite dependent on the wavelength of the incident radiation, increasing as the wavelength decreased; radiation with wavelengths shorter than 3000\AA was observed to be significantly more damaging. The irradiation system allowed different areas of any sample to be exposed simultaneously to different wavelength bands and, therefore, enabled the detection of damage as a function of photon energy.

McCargo *et al.* (Reference 3), experimenting with $\text{ZnO}/\text{K}_2\text{SiO}_3$ and $\text{La}_2\text{O}_3/\text{K}_2\text{SiO}_3$ as thermal control coatings, observed that more damage resulted from filtered electromagnetic radiation with wavelengths less than 4000\AA from a xenon source than from radiation with wavelengths greater than 4000\AA . His results qualitatively substantiated those of Arvesen.

Swofford, Mangold, and Johnson (Reference 4) undertook an experimental investigation of the amount of degradation resulting from the irradiation of thermal-control coatings with α (solar absorptance) = 0.25, using radiation in the band from 2000\AA to 500\AA . Damage incurred by 2000\AA to 900\AA radiation was of the same order of magnitude as that incurred by 4000\AA to 2000\AA radiation. Also, coatings exposed to 2000\AA to 500\AA radiation exhibited more damage than those exposed to 2000\AA to 900\AA radiation. It remains to be shown,

*Colony, Joe A., "The Preparation and Space Environment Behavior of a Silicate-Treated Zinc Oxide Thermal Control Coating-101", NASA Goddard Space Flight Center Document X-713-70-194, May 1970.

therefore, that radiation in the interval from 900Å to 500Å is especially damaging. These results, however, substantiate the Arvesen investigation; they provide only limited qualitative data, since the energy and wavelength parameters were not carefully controlled or defined. Consequently, any attempts to explain the mechanisms from these data are premature.

Arvesen (Reference 2) further concluded from his experiments that the relative spectral sensitivity of his coatings was virtually independent of intensity and that the effect of total dose (intensity \times time) was constant. Our investigations revealed that the effects of exposure time, intensity, and dose produce independent sets of data.

The effects of ultraviolet radiation of various wavelengths, intensities, and durations on the infrared reflectance of ZnO-silicone coatings were studied to clarify the relative importance of intensity and dose as parameters and to obtain further insight into the nature of reflectance degradation. The coating sample under examination was composed of zinc oxide (New Jersey Zinc Co. SP-500) and methyl silicone resin (General Electric Co. RTV-602), combined with toluene and a tetramethyl ammonium hydroxide catalyst. When this coating was irradiated with ultraviolet light at constant intensity for various intervals of time, the rate of damage was an exponential function of the time. This held true for each new intensity and time interval. When the exposure time was held constant, the damage varied with the intensity of illumination, I , as the sum of terms containing \sqrt{I} and I .

Because of the scatter of the data points, a precise relationship could not be obtained between the damage and the total dose. As indicated before, the effect of total energy dose could not be treated as constant for our data.

APPARATUS

The apparatus used in these experiments consisted of four major components: a vacuum system, a high-intensity monochromator, a spectroreflectometer, and a high-intensity xenon lamp.

The vacuum system included a liquid-nitrogen-cooled sorption pump for roughing, a Varian 8 l/sec Vac-ion pump that provided working pressures of from 1×10^{-6} to 1×10^{-8} torr, and a radiation cell with a supersil quartz window where the sample was positioned during evacuation, irradiation, and measurement. The sample was aligned perpendicular to the beam, flat against the inside surface of the window.

Radiation with any wavelength from 7000Å to 2000Å could be selected with the high-intensity Bausch and Lomb monochromator. The entrance and exit slits were adjusted to provide a large enough area for measurement of resultant damage at the sample position.

A Beckman DK-2A spectroreflectometer, with a range from 24,000Å to 3000Å, was used to measure the spectral reflectance of the sample. When a measurement was desired, the entire vacuum system was moved to place the quartz window flat against the integrating sphere port.

The source of irradiation was a high-pressure, 150-W, Eimac xenon lamp with an internal rhodium reflector. It was ideal for these experiments because of its high output of short wavelength radiation. This

was delivered, within 3 deg of the beam axis, on the monochromator input slit. Thus, high-intensity, narrow-band radiation could be focused on the sample over an area sufficient for reflectance measurements.

TEST PROCEDURE

The absolute energy distribution and bandwidth of the radiation from the monochromator (Appendix A) were determined by use of a Cary Model 14 spectrophotometer which utilized a standard tungsten lamp.

Intensity measurements were made at the sample position with a special flat-response, high-sensitivity, Epply thermopile. Although the maximum intensity was detected at 2600Å with the monochromator and thermopile, the absolute measurement revealed that the wavelength of maximum intensity actually occurred at 2500Å, with lesser peaks located at 2685Å and 2350Å.

By using the planimeter, 97 percent of the radiation beam was calculated to be within a $\pm 200\text{\AA}$ bandwidth of 2600Å.

The sample was attached to a sample holder and the cell was evacuated to at least 10^{-6} torr with the aid of the liquid-nitrogen-cooled sorption pump. After the infrared reflectance of the sample was measured (Figure 1), it was exposed (Figure 2) to the desired ultraviolet radiation at the selected intensity for a predetermined amount of time before the reflectance was measured again. The wavelength of 19,500Å was chosen for data compilation because maximum sensitivity to damage was observed there. All reflectance measurements were *in situ*; that is, the vacuum environment was retained while the various measurements were performed.

RESULTS AND DISCUSSION

The damage dependent on the wavelength, as shown in Figure 3. Degradation increased from 3500Å to 2200Å. The curve indicates that most of the damage due to the radiation occurs considerably below the edge of the ultraviolet-radiation band (3800Å). Unfortunately, insufficient energy at shorter wavelengths prohibited the extension of this investigation, and a maximum damaging wavelength, such as the one reported by Donohoe (Reference 5) for anodized aluminum, has not yet been detected.

Time and intensity relationships were investigated in the bandpass $2600\text{\AA} \pm 200\text{\AA}$ because considerable damage occurred there, and also because a wide range of intensities was available. The damage increased as a function of time, as shown in Figure 4 for three constant intensities of radiation. In each case, the damage is an exponential function of time, and the optical effect, damage per unit time, steadily decreases. Over the limited time range considered here, these curves can be described by the relationship

$$\Delta r(I, t) = \Delta r_1(I)(1 - e^{-t/\tau}), \quad (1)$$

where

Δr = change in reflectance

and

$$\Delta r_1(I) = K_1 \sqrt{I} + K_2 I.$$

Figure 4 also shows points calculated from this relationship with $\tau = 0.55$ hours so that they may be compared with laboratory data.

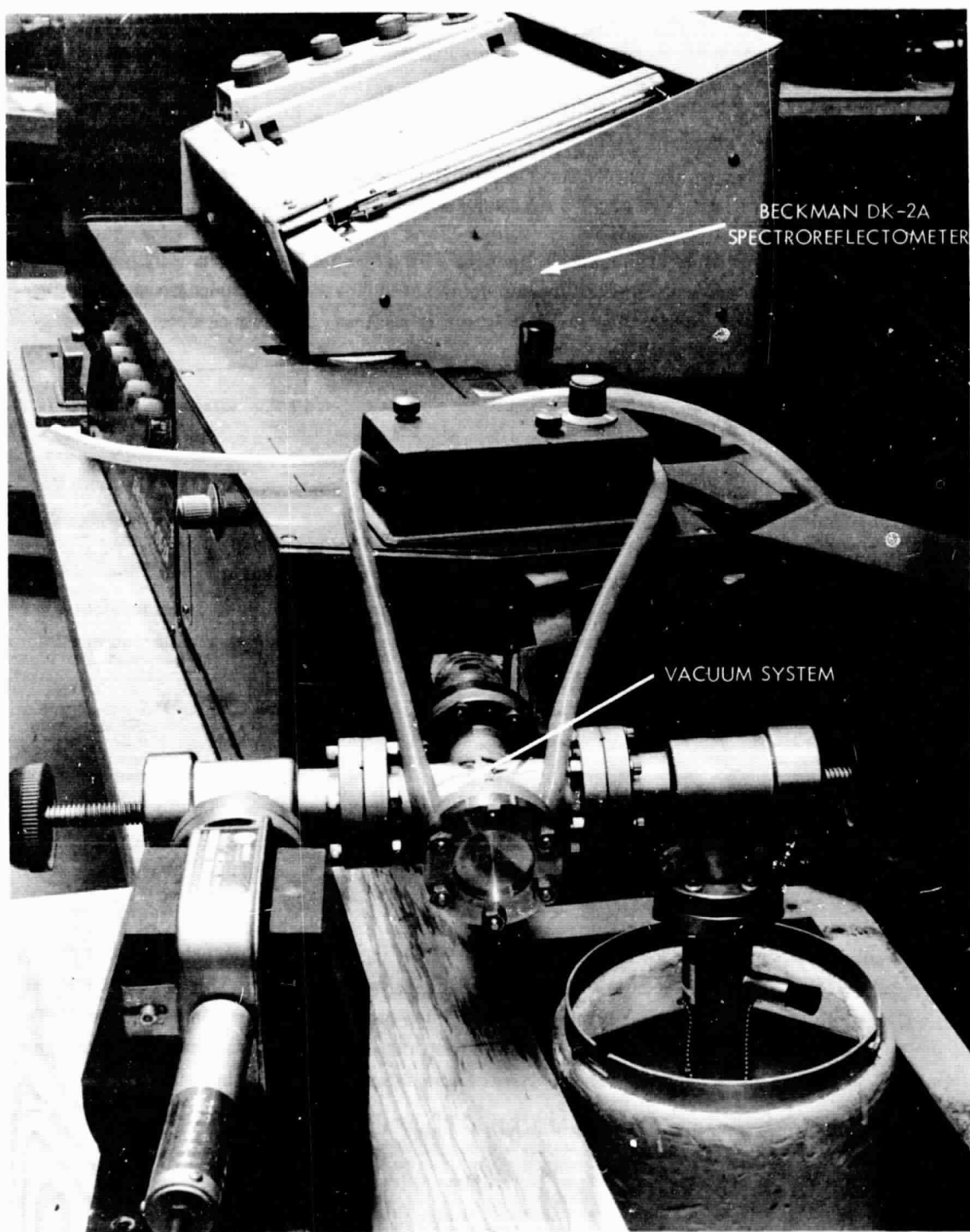


Figure 1—Apparatus for measurement of spectral reflectance of samples.

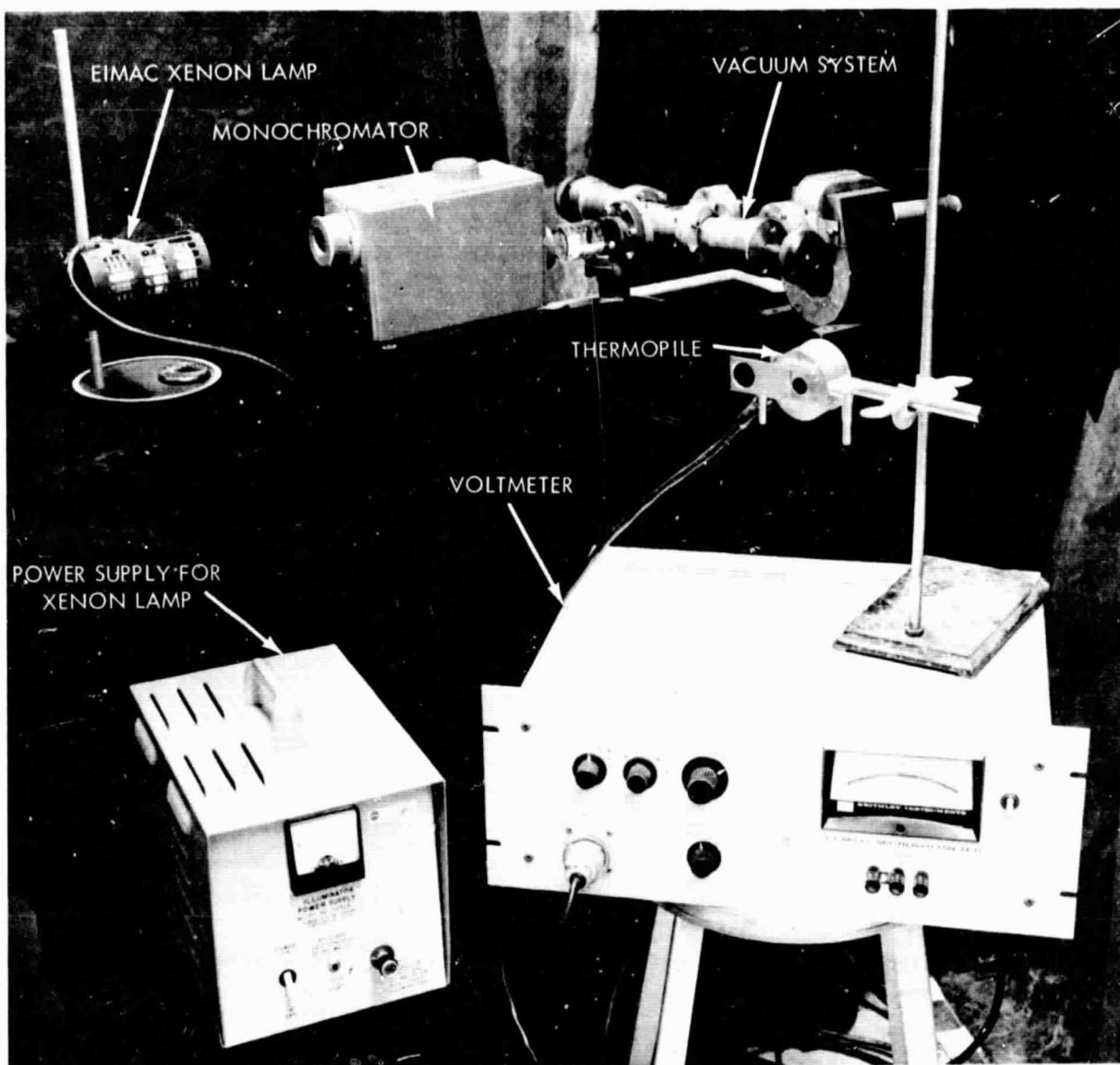


Figure 2—Apparatus for ultraviolet irradiation of samples.

When the data were replotted, with damage expressed as a function of intensity and with the time of exposure held constant, another simple relationship was observed (see Figure 5). Specifically, the change in reflectance at $19,500\text{\AA}$ was seen to be proportional to the square root of the intensity after 4 hours of exposure:

$$\Delta r_2(I) = K_1 \sqrt{I}, \quad (2)$$

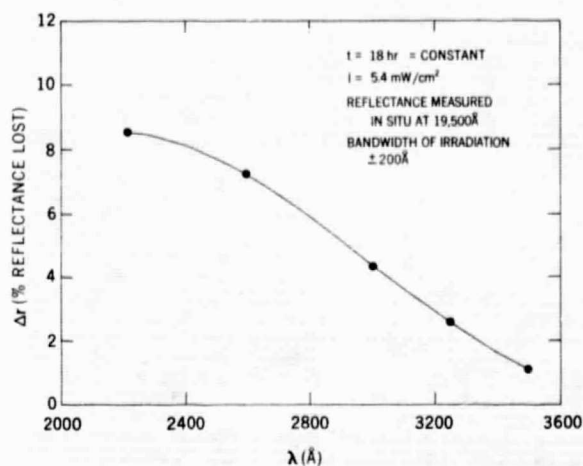


Figure 3—Wavelength dependence of infrared reflectance damage at constant dose, 97 (mW-hr)/cm².

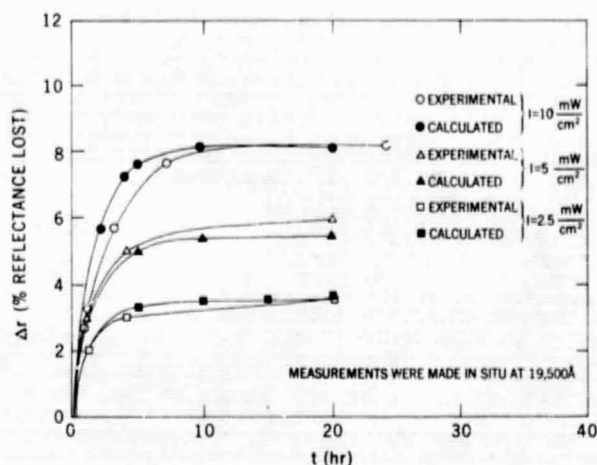


Figure 4—Time dependence of infrared reflectance damage, $\lambda = 2600 \text{ \AA}$.

with $K_1 = 2.00 (\text{mW}/\text{cm}^2)^{-1/2}$. When the coating had been exposed for 20 hours, however, the degradation could be viewed as the sum of the four-hour curve and a term proportional to I , so that now

$$\Delta r_1(I) = K_1 \sqrt{I} + K_2 I, \quad (3)$$

where $K_2 = 0.185 (\text{mW}/\text{cm}^2)^{-1}$. Overall, the data indicate the relationship

$$\Delta r(I, t) = (K_1 \sqrt{I} + K_2 I)(1 - e^{-t/\tau}). \quad (4)$$

Figure 5 also shows points calculated with the specified constants for all curves.

A possible explanation for this behavior is that, after four hours of exposure, another process became evident. The first-power intensity function may be attributed to the binder, and the square-root intensity function may be attributed to electron-hole generation in ZnO (Reference 6).

The change in reflectance was plotted as a function of total dose ($I \times t$) (Figure 6). From the scatter of the data points, it is apparent that no simple relationship exists.

CONCLUSIONS

The results of an experimental investigation indicate that the rate of damage by ultraviolet radiation to a ZnO-silicone coating is a function of wavelength, intensity, dose, and time. The degradation rate increased as incident radiation wavelength decreased from 3500 Å to 2200 Å. It was also observed that this rate is proportional to the square root of the illumination intensity for 4 hours of irradiation and to the sum of square root and first power terms for 20 hours of exposure. When damage was plotted as a function of time for constant intensities, an exponential function was obtained. It was also shown that the effect of total dose should not be considered constant, as many investigators have assumed. Instead, it is affected independently by intensity and time.

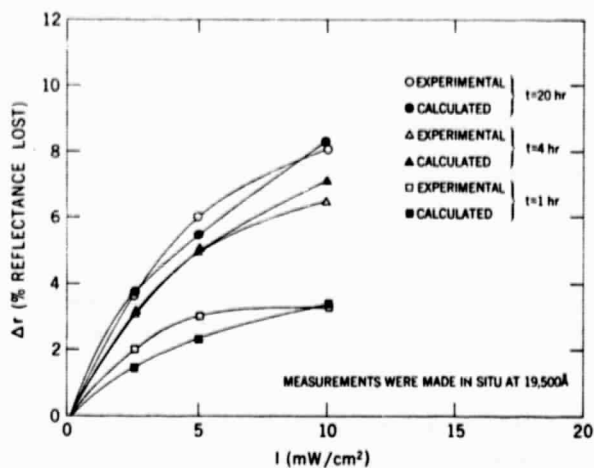


Figure 5—Intensity dependence of infrared reflectance damage, $\lambda = 2600\text{\AA}$.

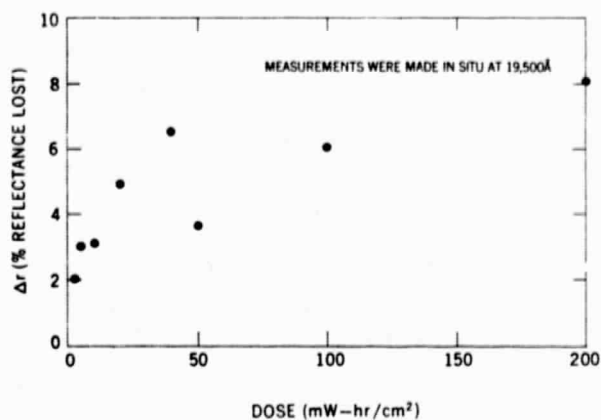


Figure 6—Absence of simple relationship between degradation rate and dose, $\lambda = 2600\text{\AA}$.

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Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, Maryland, December 4, 1970
124-09-26-15-51

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Appendix A
Bandwidth Determination

